

IPST Technical Paper Series Number 518

Bleaching of Kraft Pulps via Dioxiranes

A.J. Ragauskas

March 1994

**Submitted to
Advances in Oxygenated Processes**

Copyright® 1994 by the Institute of Paper Science and Technology

For Members Only

Bleaching of Kraft Pulps via Dioxiranes

Arthur J. Ragauskas, Assistant Professor of Wood Chemistry

Institute of Paper Science and Technology, Atlanta, GA 30318

INTRODUCTION

Manufacturing of pulp and paper is a large and complex process, employing a variety of technologies.¹ The ultimate goal of these operations is the conversion of lignocellulosic fibers into paper and paper-board products. Of the variety of paper products manufactured, the production of high-brightness, high-strength products requires some of the most sophisticated technologies available. In general, these pulps can be manufactured either by retaining the three major constituents of wood: lignin, hemicellulose, and cellulose, or by selectively removing lignin to yield a cellulosic-based fiber for paper-making. Regardless of which process is employed, both of these types of pulps require chemical treatments to increase the brightness properties of the final product. Pulps which retain lignin are frequently referred to as mechanical pulps, and although these pulps can be bleached to relatively high-brightness values, their well-known propensity to undergo photo- and thermal-yellowing has limited their application for high-value paper products.²

Since lignin is the main coloring component of lignocellulosic fibers, its removal by chemical processes yields a much brighter product. Furthermore, the yellowing properties of mechanical pulp are initiated by lignin, and its removal substantially improves

the photo- and thermal-stability properties of these pulps.³ The production of lignin-free pulps, frequently referred to as chemical pulps, is achieved through a series of chemical processes which remove lignin without seriously degrading the carbohydrate fraction. Although several commercial technologies are available to delignify wood fibers, in North America, the most frequently employed process utilizes sodium hydroxide and sodium sulfide. This procedure, known as the kraft pulping process, delignifies wood fibers through a series of hydrolytic and sulfidolytic reactions at elevated temperatures.⁴ Upon completion of the chemical cook, approximately 95% of the lignin has been removed. The remaining lignin is resistant to these cooking conditions and must be removed through a series of oxidative bleaching reactions.

Although the chemical structure of residual lignin remains poorly defined, it is commonly believed that this type of lignin is enriched with vinyl ether-⁵ and stilbene-⁶ type structures (**A**), condensed lignin⁷ (**B**), lignin/carbohydrate complexes⁸ (**C**), and trace amounts of β -O-aryl ether linkages⁹ (**D**) (see Figure 1). Structures **A**, **B**, and **C** are stable to alkaline pulping conditions, and therefore, removal of these components is achieved with the use of chemical reagents which can oxidatively fragment the lignin polymer and introduce hydrophilic groups, such as carboxylates, and hydroxy and phenoxy groups.

In the 19th century, this was accomplished using two stages of hypochlorite treatment.¹⁰ This process was improved in the early 1900s when it was shown that the use of an alkaline extraction stage between the two hypochlorite treatments and intermediate

washing substantially reduced the amounts of chemical required for bleaching and yielded stronger and brighter pulps.¹¹ Subsequent investigations in bleaching chemistry herald the use of chlorine and chlorine dioxide as the preferred bleaching agents for chemical pulps. By the late 1950s, the basic bleaching agents for chemical pulps had been determined. These oxidative treatments remained the mainstream of the pulp and paper industry until the late 1980s.¹²

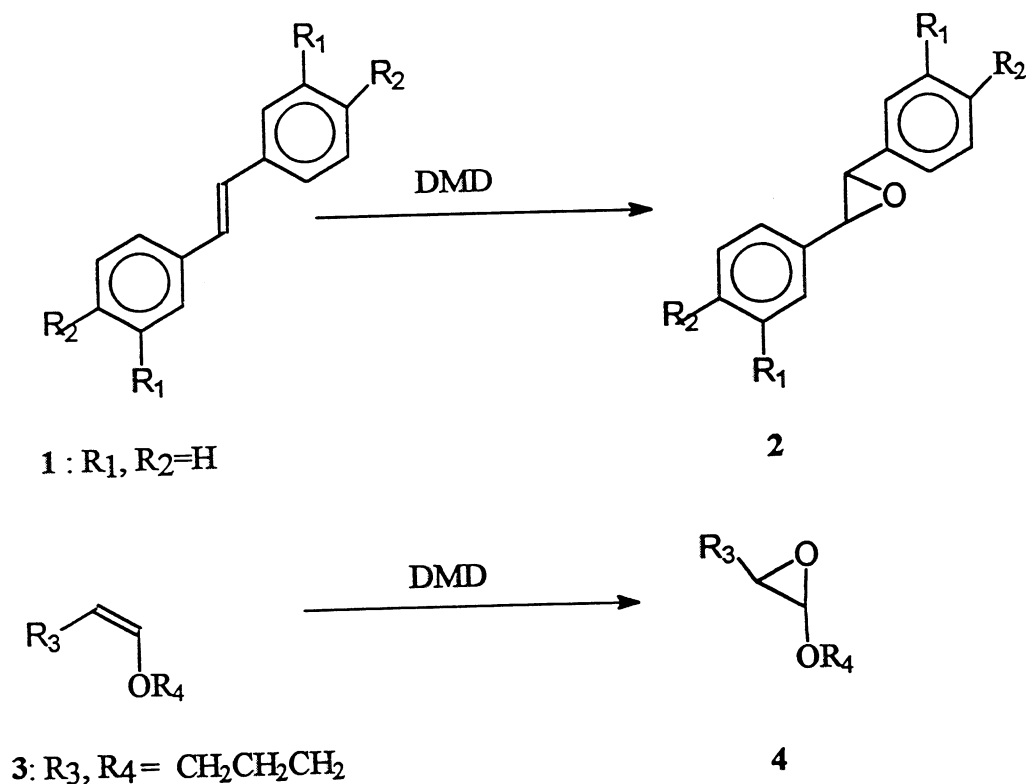
Historically, the effluents generated from pulp bleaching operations were discharged in aquatic systems with minimal secondary treatment. As bleaching operations grew in capacity, these effluents began to impact upon regional aquatic systems. As a result, a variety of secondary treatment systems were built to properly treat bleach plant effluents.¹³ The detection of polychlorinated dibenzo-p-dioxins and dibenzofurans in bleach plant effluents in 1987 dramatically altered public concern about these effluents.¹⁴ In response to these concerns, process changes were rapidly implemented which virtually eliminated dioxin discharges.¹⁵ Nonetheless, these concerns were only a prelude to a greater societal awareness of the impact that industrial practices have on the environment. Indeed, the use of chlorine-based agents not only in the pulp and paper industry, but for almost all industrial processes has come under increasing environmental scrutiny.¹⁶ Consequently, a variety of nonchlorine-based oxidative reagents have been examined as potential alternatives for bleaching chemical pulps. To date, the only commercial pulp bleaching alternatives to chlorine and chlorine-dioxide are hydrogen peroxide,¹⁷ ozone,¹⁸ and alkaline oxygen treatments.¹⁹ Despite these successful developments, there remains

a strong need to develop alternative bleaching chemicals which could displace current chlorine-based bleaching technologies. Therefore, USA researchers at the Institute of Paper Science and Technology, and University of Missouri, and Paprican, in Canada, have begun to investigate the potential bleaching capabilities of dimethyldioxirane (DMD).

Basic Bleaching Chemistry of Dimethyldioxirane

The application of dimethyldioxirane as a bleaching agent for chemical pulps was attractive based on two basic considerations. First, a review of dimethyldioxirane chemical reactivity²⁰ suggested that this cyclic peroxide would have unique oxidative properties toward lignin. Second, the reagent can be prepared from hydrogen peroxide, sulfuric acid, and acetone which suggests that the on-site generation costs of dimethyldioxirane could be minimal.²¹

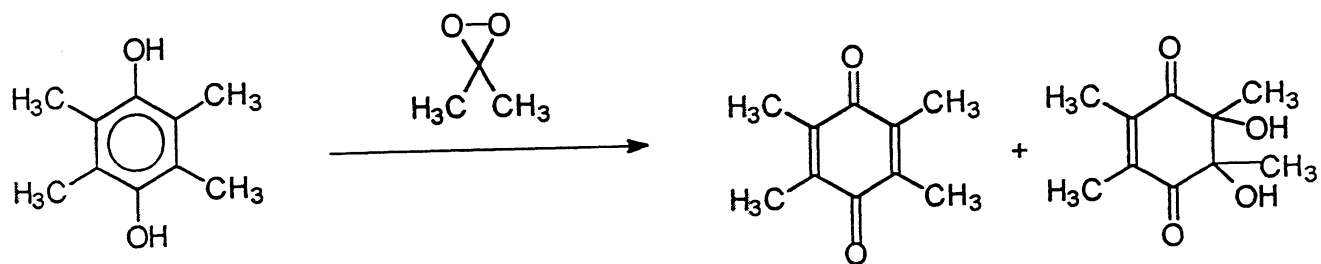
Although there have been no reported studies directed at examining the fundamental bleaching chemistry of dimethyldioxirane to date, several publications are suggestive of the chemical reactivity of dimethyldioxirane with lignin-like structures. As discussed, residual lignin is believed to be enriched in vinyl ether and stilbene structures which would most likely react with DMD. Baumstark and Vasquez²² have previously demonstrated that the reactivity of DMD with simple stilbene derivatives (**1**) yields the corresponding epoxide (**2**), and analogous results have been reported by Harris et al.²³ for vinyl ether-type structures (i.e., **3** → **4**) as highlighted below.



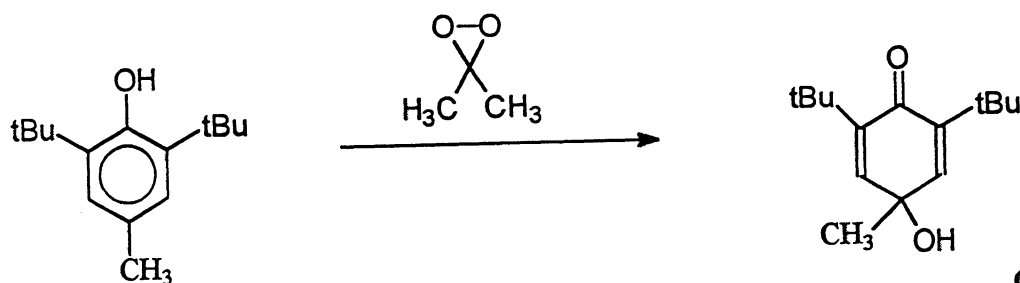
Based on these results it was anticipated that lignin-like analogues of compounds **1** and **3** would also undergo epoxidation via DMD and these products could then be hydrolyzed during caustic extraction. The overall result of these series of reactions would be to increase the hydrophilic nature of the oxidized lignin.

Early studies by Murray²⁴ demonstrated the ability of DMD to epoxidize electron-rich aromatic systems such as pyrene and naphthalene. Adam²⁵ and Crandall²⁶ have also reported that dimethyldioxirane is capable of oxygen transfer into hydroquinone structures

as highlighted below.



Adam et al.²⁵

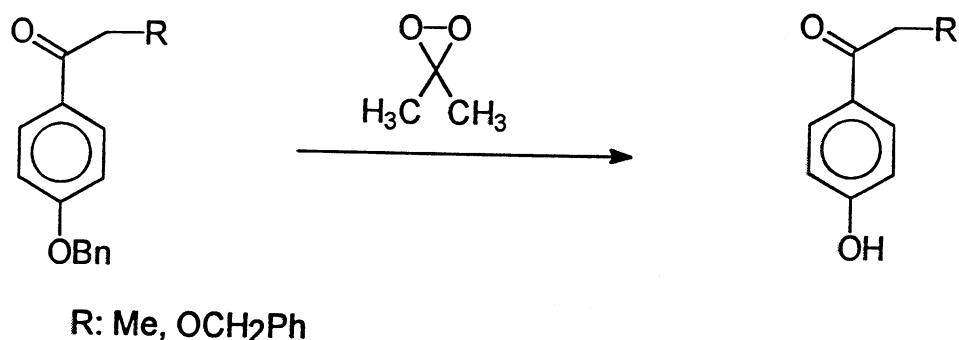


Crandall et al.²⁶

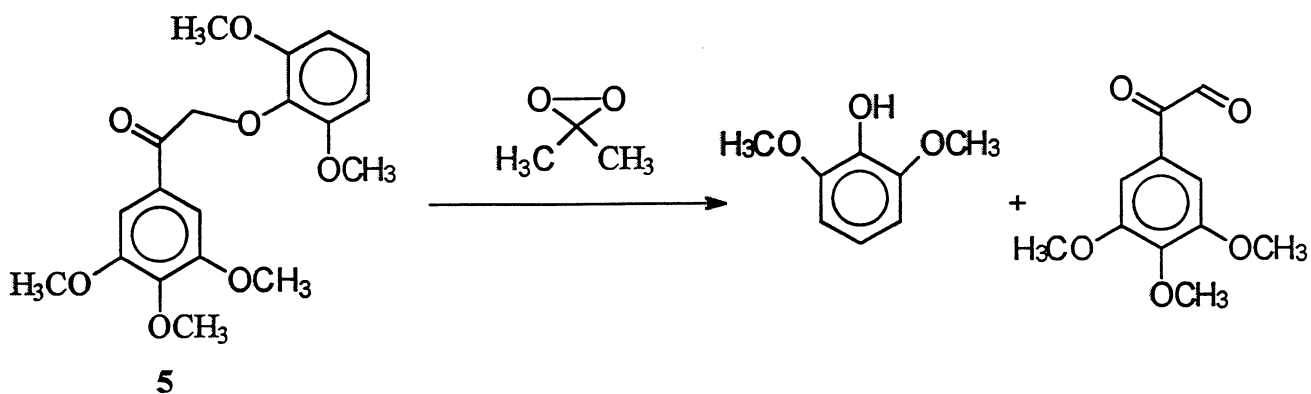
These results suggest that dioxirane-based bleaching agents could oxidize the electron-rich aromatic units of lignin which are derived from p-coumaryl, p-coniferyl, and p-sinapyl alcohol.²⁷ The ability to introduce additional hydroxy groups into the aromatic subunits of lignin would enhance the solubility of oxidized lignin fragments in an alkaline extraction step.

The ability of simple dioxiranes to insert into carbon-hydrogen bonds has also been

shown to occur.²⁸ Marples et al utilized this reaction to debenzylate several benzylated structures, as shown below.²⁹



Preliminary studies in the author's laboratory demonstrated that analogous reactions occurred with lignin-like structures; the oxidative cleavage of **5** is representative of this type of reaction.³⁰



The ability of DMD to cleave inter-lignin linkages was suggestive of the unique bleaching capabilities that substituted dioxirane could well exhibit.

Finally, studies by Danishefsky³¹ have shown that DMD has an exceptionally low reactivity with fully-saturated carbohydrate derivatives. These results suggest that DMD could be a very selective bleaching reagent for kraft pulp, oxidatively removing lignin without seriously damaging cellulose and the assorted hemicellulose polymers found in wood fibers.

Just as the renaissance in dioxirane chemistry was made possible by Murray's²¹ simplified acetone-carbate method to prepare dimethyldioxirane, the simplicity of this method has made it possible to consider commercial bleaching applications. Figure 2 summarizes the general chemical reactions involved in the preparation of dimethyldioxirane and its applicability for bleaching chemical pulps. It should be noted that acetone is not consumed during these reactions and acts as a true catalyst transferring oxygen from peroxymonosulfate to an oxidizable substrate. The catalytic properties of acetone have practical considerations as this reduces the amount of acetone needed for bleaching chemical. Furthermore, the incorporation of an acetone recovery stage after the DMD bleaching stage would reduce the overall chemical costs of bleaching with dimethyldioxirane.

For pulp bleaching operations, cost considerations prohibit the use of commercial

caroate, available as a triple salt of $2\text{KHSO}_5 \bullet \text{KHSO}_4 \bullet \text{K}_2\text{SO}_4$ (commercial trade name OxoneTM), as the source of peroxymonosulfate. Instead, it is anticipated that the caroate salt will be prepared on-site by combining 96% sulfuric acid with a 70% hydrogen peroxide solution. The technology needed to generate caro's acid from these reagents is already available and could be incorporated into modern pulp bleaching operations.³²

In summary, the oxidative chemistry of DMD and its methods of generation appeared to be very attractive for commercial applications. Over the last three years, substantial progress has been achieved in developing the bleaching capabilities of dimethyldioxirane for chemical pulps. The remainder of this paper will summarize these accomplishments.

PULP BLEACHING STUDIES

The intrinsic bleaching capabilities of DMD were initially assessed independently by Murray and Lee at University of Missouri/Paprican³³ and Ragauskas at IPST.³⁴ Employing Murray's method of generating DMD,²¹ several chemical pulps were treated with varying charges of dimethyldioxirane, washed, and extracted with aqueous alkaline. The bleached and extracted pulps were characterized according to changes in lignin content, brightness, and viscosity. These parameters are the fundamental measurements by which bleaching efficiency is determined. Viscosity determinations³⁵ are a relative measure of oxidative damage to cellulose and are indicative of pulp strength properties. Lignin content is expressed in terms of a kappa number³⁶ ($\text{kappa number} \times 0.15 = \%$

lignin per gram of fiber) and is readily determined by KMnO_4 titration of the pulp fibers. Brightness values are measured on dry testsheets by irradiating the handsheets with 457 nm reference light and measuring the percent reflectance.³⁷

As shown in Table 1, treatment of kraft pulps with DMD/acetone solutions led to extensive delignification of the pulps and accompanying brightness gains. Studies by Lee demonstrated that the DMD-bleached hardwood kraft pulp also exhibited superior strength properties to that of the same pulp delignified by oxygen to the same lignin level. Furthermore, the DMD-bleached pulps responded favorably with chlorine dioxide to yield high-brightness pulps. A comparison of these preliminary studies with well-known literature results suggested that the bleaching capabilities of DMD were comparable to chlorine and/or chlorine dioxide.³³

Although these results were promising, the methods employed to generate and isolate acetone/DMD solutions were clearly not suitable for commercial applications. To address these issues, research activities by Lee and Ragauskas were directed towards developing in-situ DMD bleaching procedures. Initial studies by Lee and Murray^{33,38} demonstrated that the addition of OxoneTM (Note: OxoneTM was employed as a convenient source of peroxymonosulfate) to an acetone/water pulp slurry buffered to pH 7.0, generated DMD in-situ and resulted in extensive delignification of a hardwood kraft pulp. As summarized in Figure 3, DMD delignification of the kraft pulp was accompanied with only minor losses in viscosity.

The bleaching properties of in-situ generated DMD were also explored by Ragauskas.³⁴ Initially, the bleaching efficiency of peroxymonosulfate was evaluated employing aqueous acetone and water as bleaching solvents. The differences in extent of delignification for the water and aqueous acetone bleaching systems are shown in Figure 4. These studies clearly demonstrate that the bleaching properties of peroxymonosulfate were substantially improved when the bleaching solvent was a mixture of acetone and water. The use of an acetone/water mixture not only improved the extent of delignification, but these benefits were accomplished without substantial oxidative damage to the cellulose fibers, as summarized in Table 2. To insure that the differences observed in Figure 4 could be attributed to bleaching chemistry and not to differences in solubility of the oxidized lignin, Ragauskas employed several post-bleaching washing treatments for the control pulps. After bleaching, the control pulps were washed with water, then extracted with an acetone/water solution and re-washed with water. In summary these preliminary results suggested that in-situ generated DMD could be a very selective and effective bleaching reagent.

As expected, the extent of delignification was also shown to be sensitive to the relative amounts of water and acetone present during in-situ DMD bleaching procedures. During preliminary studies by Ragauskas³⁴, the mass ratio of acetone to pulp (oven dry weight) was maintained at 10:1. Research studies by C.-L. Lee et al.³⁹ demonstrated this ratio could be reduced to 0.16:1.0; further reductions in acetone substantially reduce the bleaching efficiency of this procedure.

As an alternative to employing aqueous acetone pulp slurries for the bleaching reactions, the effect of premixing the bleaching reagents has also been examined. After analyzing a series of premixing conditions, the optimal procedure employed a 4:1 mass ratio of acetone to pulp (oven dry weight). The bleaching reagents were premixed for 5 minutes prior to addition to the aqueous pulp slurry. After establishing a simplified, in-situ method of generating and bleaching with DMD, Ragauskas studied the effects of reaction time, pH, and temperature.⁴⁰ As summarized in Table 3, in-situ DMD bleaching of kraft pulps was shown to be completed within 1 hour, at room temperature. DMD bleaching reactions were also shown to be sensitive to temperature as illustrated in Figure 5, and improved delignification responses were shown to occur at higher temperatures.

Although the optimal pH for DMD generation is between 7.0-7.5, the pH profile for bleaching kraft pulps was initially an unknown factor. Employing in-situ, premixed DMD solutions, Ragauskas demonstrated that the bleaching chemistry of DMD was also pH sensitive. As summarized in Figure 6, the optimal pH for DMD delignification of kraft pulps was shown to be at ca pH 7.0. Whether these results are due to preferred DMD bleaching kinetics or perhaps due to reduced rates of re-generating the dioxirane catalyst remains to be determined.

As these preliminary studies came to a conclusion, it was apparent that in-situ generated DMD offered unique capabilities to bleach kraft pulps. Research efforts have therefore been directed at assessing several other process variables which would be of importance

for any future commercial applications, including sensitivity of DMD to transitional metals, potential use of alternative dioxirane structures, and bleaching sequence studies.

Trace Metals

As the pulp and paper industry increases its reliance on oxygen-based bleaching reagents, the need to control the metals profile of the incoming pulps has become an important issue.⁴¹ It is well known that the presence of metals in wood fibers (see Table 4), chelated principally by lignin, can be very detrimental to oxygen-based bleaching reagents, such as hydrogen peroxide and ozone.⁴² A variety of studies have shown that several trace metals, including iron, manganese and nickel can decompose hydrogen peroxide into hydroxy radicals.⁴³ This radical has a very poor selectivity between lignin and cellulose and therefore cause extensive oxidative damage to cellulose, thereby reducing its degree of polymerization and its intrinsic strength properties. Comparable deleterious effects have been noted between transitional metals and the bleaching chemistry of ozone and peroxymonosulfate.⁴⁴ The generation of dimethyldioxirane has also been shown to be sensitive to transitional metals.⁴⁵ These results suggest that the bleaching chemistry of DMD could also be influenced by the presence of metals.

To evaluate the impact of trace metals on DMD bleaching of kraft pulps, Ragauskas prepared a series of chelated and non-chelated pulps, treated each with DMD, and monitored the extent of delignification.⁴⁶ Removal of metals was accomplished employing standard EDTA chelation procedures⁴⁷ and sulfuric acid washing methods.⁴⁸ Following

these treatments, the pulps were analyzed for metal contents employing standard AA procedures. Although both procedures were effective at reducing the metals present in the kraft pulp, it is apparent that EDTA was slightly more effective at removing iron salts. Once the pulps had been chelated and characterized, each sample was bleached with DMD (0.7% charge of distilled DMD; see Table 5 for more details) and then extracted with aqueous alkaline. The results of these studies clearly demonstrate that the bleaching efficiency of DMD is affected by trace metals. A comparison of the bleached/extracted EDTA pulp, sulfuric acid washed pulp, and non-chelated pulp indicates that the chelated pulps have undergone further delignification. These results have been attributed to the reduced presence of metals which could interfere with DMD's bleaching reactions. A comparison of the metals profile for the EDTA and sulfuric acid washed pulps suggested that the presence of iron in the pulp fibers has a detrimental impact on bleaching efficiency. Ongoing studies will establish which metals are most harmful to the bleaching chemistry of DMD. Furthermore, the results of these studies pose interesting mechanistic questions which are currently under study in the author's laboratory.

Alternative Dioxiranes

Although most reported dioxirane bleaching studies have focused on the bleaching efficiency of dimethyldioxirane, there are no theoretical reasons why alternative dioxiranes could not be successful at bleaching kraft pulps. Indeed, an examination of the literature suggests that DMD may well be one of the least reactive dioxirane species.⁴⁹ To explore this issue, the potential bleaching chemistry of peroxymonosulfate in the presence of

either cyclohexanone, cyclopentanone, or 2-butanone have been examined by Ragauskas.⁵⁰ Following the same procedure employed to generate DMD, the alternative ketone bearing structures were treated with peroxymonosulfate, sodium bicarbonate, and water. The resulting mixture was added to a softwood kraft pulp and stirred for 1 hour. The bleaching efficiency of each of these mixtures was then monitored by determining the extent of delignification. As summarized in Table 6, the bleaching efficiency of 2-butanone/peroxymonosulfate was nearly as efficient as DMD at removing lignin from kraft pulps. In comparison, the bleaching mixture derived from either cyclohexanone or cyclopentanone and peroxymonosulfate appeared to be relatively unreactive with kraft pulps. These latter results were attributed to unfavorable solubility conditions for generating this dioxirane. This possibility was further explored by repeating the dioxirane bleaching procedure with a phase transfer reagent to aid in the generation of the substituted dioxirane generated from cyclopentanone. The use of a phase transfer catalyst for generating substituted dioxiranes from ketones with limited water solubility has been successfully developed by Curci.⁵¹ Unfortunately, the resulting procedure did not assist in improving the bleaching properties of cyclopentanone and OxoneTM which are presumably due in part to the solubility problems.

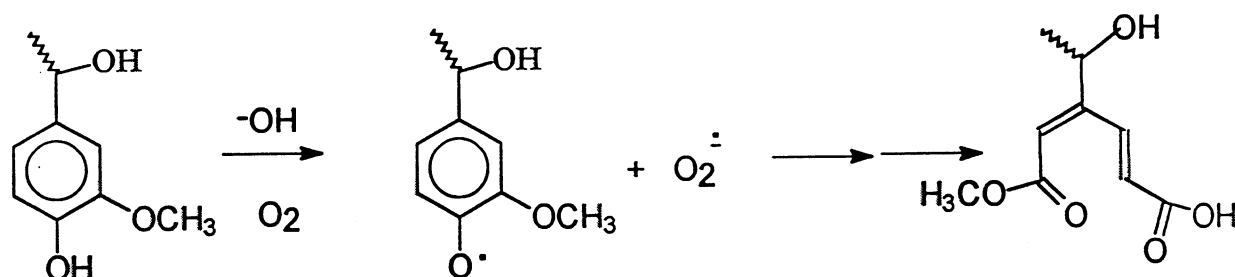
Although the bleaching results achieved from 2-butanone and OxoneTM were promising, we have been unable to find a dioxirane precursor which substantially outperforms DMD. In light of these considerations and the cost advantages of employing acetone, it appears that DMD may well be the preferred dioxirane structure for bleaching kraft pulps.

DMD-Bleaching Sequences

The bleaching of chemical pulps is a multi-step process involving several oxidative treatments, washing procedures, and alkaline extractions. The complexity of this process can vary immensely from employing just one bleaching chemical several times to coupling the oxidative bleaching properties of several reagents. For example, many modern bleaching operations are currently employing three oxidative chlorine dioxide treatments coupled with alkaline extractions after the first two bleaching stages. This sequence is referred to as a DEDED sequence. (Note: Bleaching sequences are frequently described by coupling together the symbols for each bleaching stage; see Table 7 for a complete listing of bleaching abbreviations).

Multi-stage bleaching operations are required since it is not possible to bleach kraft pulps to high-brightness values in a single step. Each bleaching stage has a response curve with respect to chemical charge, and at lower chemical charges, the amount of lignin removed is linear with the amount of bleaching chemical applied. At some point in the curve, this linear relationship fails, and the efficiency of delignification begins to decrease, eventually reaching a point where additional amounts of bleaching chemical is of little or no benefit.⁵² The typical response curve for chlorine dioxide charge versus brightness development is shown in Figure 7. Based upon these considerations alone, the production of fully-bleached kraft pulps would require several treatments with DMD and/or the use of alternative bleaching reagents.

In addition to these considerations, when utilizing several bleaching agents, the sequence by which these chemicals are applied onto pulps influences the final outcome. For example, when using ozone, chlorine dioxide, and oxygen delignification (i.e., $O_2/NaOH/H_2O$) for bleaching kraft pulps, the final brightness and strength properties are vastly improved when OZED is the bleaching sequence instead of ZOED. These results can be readily explained in terms of lignin bleaching chemistry. The mechanism of oxygen delignification is principally due to the attack of O_2 on a phenolate anion, as shown below.⁵³



Bleaching of kraft pulps with ozone prior to oxygen delignification removes most of the free phenoxy groups. This reduction in the phenoxy group content of lignin reduces the bleaching efficiency of the oxygen delignification.

In light of these considerations, the development of DMD as a bleaching agent for kraft

pulps will require extensive bleaching sequence studies. Recent studies by C.-L. Lee et al.³⁹ and McDonough et al.⁵⁴ have begun to explore these issues. Some of their results are summarized in this section.

Bleaching sequence studies by C.-L. Lee have demonstrated that DMD is a very versatile bleaching agent which can be employed in conjunction with either chlorine dioxide, hydrogen peroxide, or oxygen delignification. DMD was shown to be an excellent replacement for the first stage of a (C/D)EDED sequence to afford (DMD)EDED. Pulps bleached with the latter sequence exhibited higher final brightness values and improved strength properties. These properties were shown to be due to the highly efficient and selective bleaching properties of DMD. Totally chlorine-free bleached pulps have also been prepared employing either O(DMD)EP or (DMD)EP as bleaching protocols. These sequences were shown to be effective in bleaching hardwood kraft pulps to acceptable commercial brightness levels.

McDonough et al.⁵⁴ have further explored the bleaching capabilities of DMD for softwood kraft pulps. They demonstrated that the optimal placement of DMD should be early in the bleaching sequence. Employing an oxygen-delignified softwood kraft pulp, two sequences were examined with DMD, ethylenediaminetetraacetic acid (Q-stage: removes metals by chelation), and hydrogen peroxide. The sequences evaluated were O(DMD)QP, in which the DMD stage is primarily a delignifying stage, and OQP(DMD), in which DMD assumes a brightening role. Chemical charges and bleaching conditions

were identical for both sequences. The results of these studies indicate that DMD should not be placed at the end of a bleaching sequence since the desired brightening properties are not observed. Presumably, this is due, in part, to DMD's inability to oxidize quinoid structures which are most likely formed in-situ by DMD oxidation of lignin-derived hydroquinones. Application of DMD early in a bleaching sequence will still generate lignin quinoid structures, but these colored chromophores are then oxidatively removed with secondary bleaching chemicals, such as hydrogen peroxide or ozone.

Coupled with the development of new oxygen-based bleaching methods for kraft pulps, there have also been significant advances in the use of biotechnology for bleaching kraft pulps. One of the most important developments has been the use of xylanase as a pretreatment for chemical bleaching sequences.⁵⁵ Numerous studies have shown that the pretreatment of kraft pulps with xylanase significantly enhances the bleachability of the resulting pulp.⁵⁶ Typically, pretreatment of kraft pulps with xylanase prior to bleaching with chlorine, chlorine dioxide, and ozone yields chemical savings in the range of 15 to 25%. Furthermore, the enzyme-treated pulps frequently exhibit higher brightness and viscosity values. Figure 8 illustrates some of the practical delignification benefits achieved with xylanase pretreatment procedures when incorporated with ozone bleaching procedures.⁵⁷ These results show that the xylanase pretreatment procedure can enhance the extent of delignification which occurs with ozone. Although the mechanism of the biobleaching process remains ill-defined, it is frequently suggested that the xylanase pretreatment procedure hydrolyses surface xylans which permit the pulp fibers to swell

and thereby allow larger lignin fragments (i.e., less-oxidized) to diffuse out of the fiber during chemical bleaching procedures.⁵⁸

The application of the xylanase pretreatment procedure prior to in-situ DMD bleaching procedures is an attractive method to further enhance the bleaching efficiency of dimethyldioxirane. To explore this possibility, Ragauskas treated hardwood and softwood kraft pulp samples with xylanase.⁴⁰ The resulting pulps were then bleached with predistilled DMD. As a control, the starting pulps were treated in an analogous manner as in the xylanase pretreatment stage, but the enzyme was omitted from the treatment. These pulps were then bleached with freshly prepared DMD. The results of these bleaching experiments are summarized in Table 8. For the hardwood pulps, the xylanase pretreatment procedure provided clear benefits in terms of the extent of delignification, brightness gains, and reduced viscosity losses. For the softwood pulps, the enzyme treatment provided moderate benefits for extent of delignification and viscosity loss. The differences in the response to the xylanase treatment for the hardwood and softwood kraft pulps are, undoubtedly, due to the higher xylan content found in hardwoods versus softwoods. Nonetheless, xylanase pretreatment procedures were shown to have clear benefits for DMD bleaching sequences and provided a novel means of improving the bleaching efficiency of dimethyldioxirane.

FUTURE STUDIES

Clearly, research studies over the last few years have substantially enhanced the applicability of dioxirane chemistry for commercial applications. These successful laboratory studies will now require pilot plant and mill trials to further evaluate DMD's potential use as a bleaching agent for kraft pulps. Additional laboratory studies will also be required to understand the fundamental oxidative chemistry which occurs between DMD and lignin structures. Furthermore, at this stage in DMD's development, research efforts need to be directed toward evaluating the safety aspects of this reagent, especially as it applies in an industrial setting.

In summary, although many technical and scientific challenges remain, the success of the last few years certainly suggests that dioxirane chemistry and/or analogous reagents will impact on future pulp bleaching operations.

Table 1. Effects of Bleaching Kraft Pulps with 0.1 N Dimethyldioxirane/Acetone Solutions.^a

<u>Pulp</u>	<u>Charge of</u> <u>DMD^b</u>	<u>Kappa #</u>	<u>Degree of</u> <u>Delignification^c (%)</u>	<u>% Brightness</u> <u>Gain^d</u>
<u>Hardwood</u>				
Unbleached	-	16.4	-	-
Bleached	0.55%	3.4	79	46
<u>Softwood</u>				
Unbleached	-	39.5	-	-
Bleached	5.0%	12.5	68	40
Bleached/Extracted ^e		11.9	70	47

^afreshly prepared following Murray's procedure²¹; ^bcharge of DMD = mass of DMD (gr)/mass of dry pulp fibers (gr) %; ^c(initial pulp kappa - treated pulp kappa)/initial pulp kappa; ^d(treated pulp brightness - initial pulp brightness)/initial pulp brightness; ^epulp was treated with an aqueous 4×10^{-4} M NaOH solution for 3/4 h at RT.

Table 2. Peroxymonosulfate Bleaching Conditions and Delignification Results for Softwood Kraft Pulp.^a

<u>KHO₂SO₃ Charge</u>		<u>Solvent System</u>			
		<u>Water</u>		<u>2:1 Water/Acetone</u>	
		<u>Bleached</u>	<u>Extracted</u>	<u>Bleached</u>	<u>Extracted</u>
30%	% Delignification	18	23	33	46
	% Viscosity Loss	16	31	35	31
15%	% Delignification	-	-	28	39
	% Viscosity Loss	-	-	24	27

^asee Figure 3 for experimental detail.

Table 3. Extent of Delignification on Bleaching a Softwood^a Kraft Pulp with DMD as a Function of Bleaching Time.

<u>KHO₂SO₃ Charge</u>	<u>Bleaching Time (h)</u>	<u>Extent of Delignification</u>	
		<u>Bleached</u>	<u>Bleached & Extracted</u>
4%	1/2	22	28
4%	1	21	27
4%	14	17	24
8%	1/2	25	38
8%	1	37	47
8%	14	33	46

^ableaching solution was premixed employing 20 ml of water, 60 ml of acetone, and an equal mass amount of oxone and sodium bicarbonate; employed a 2% consistency pulp solution.

Table 4. Metals Analysis^a of Chelated and Non-Chelated Softwood Kraft Pulp.^b

<u>Pulp</u>	<u>Metals Content</u>								
	<u>Na</u>	<u>K</u>	<u>Mg</u>	<u>Ca</u>	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Ni</u>	<u>Zn</u>
Initial	156	60.3	720	4,100	14.6	35.4	47.9	n.d.	11.7
EDTA Chelated ^c	1,040	n.d.	45.3	401	n.d.	n.d.	n.d.	n.d.	26.6
2 N H ₂ SO ₄ ^d	122	16.6	5.4	n.d.	n.d.	4.15	n.d.	n.d.	16.6

n.d.: nondetect, detection limits were 0.01 mg/kg oven-dry pulp.

^a Atomic absorption analysis metals content expressed as mg metal/kg oven-dry pulp;

^b commercial softwood kraft pulp 19.7 kappa number; ^c see reference 47 for further details;

^d see reference 48 for further details.

Table 5. Effects of Chelation^a on DMD^b Bleaching of Kraft Softwood Pulp.

<u>Pulp</u>	<u>% Delignification</u>	
	<u>Bleaching</u>	<u>Bleaching/Extraction</u>
Non-chelated	19	25
EDTA Chelated	24	31
2 N H ₂ SO ₄ Washed	16	26

^asee Table 5 for experimental chelation data; ^bemployed 20 ml of 0.1 N DMD/acetone solution with 20 g of softwood kraft pulp, initial kappa #: 23.6.

Table 6. Peroxymonosulfate Delignification^a Properties Catalyzed by Acetone, Cyclopentanone, or 3-Pentanone.

Degree of Delignification Employing 100% Charge of Peroxymonosulfate		
<u>Ketone Precursor</u>	<u>In-Situ Dioxirane Bleached</u>	<u>Bleached and Extracted</u>
Acetone	80%	87%
Cyclopentanone	26%	28%
3-Pentanone	74%	79%

^aemployed a softwood kraft pulp starting kappa number: 26.3.

Table 7. Bleaching Abbreviations.

<u>Symbol</u>	<u>Bleaching Stage</u>	<u>Bleaching Agent</u>
C	Chlorination	Chlorine (Cl_2)
C/D	Chlorination	Chlorine with a small amount of ClO_2
E	Extraction	NaOH
D	Chlorine Dioxide	Cl_2O
O	Oxygen	NaOH and O_2
	Delignification	
PAA	Peracetic Acid	$\text{CH}_3\text{CO}_3\text{H}$
P	Peroxide	H_2O_2
Q	Chelation	EDTA
X	Bio-Boosting or Biobleaching	Xylanase pretreatment
Z	Ozonation	O_3

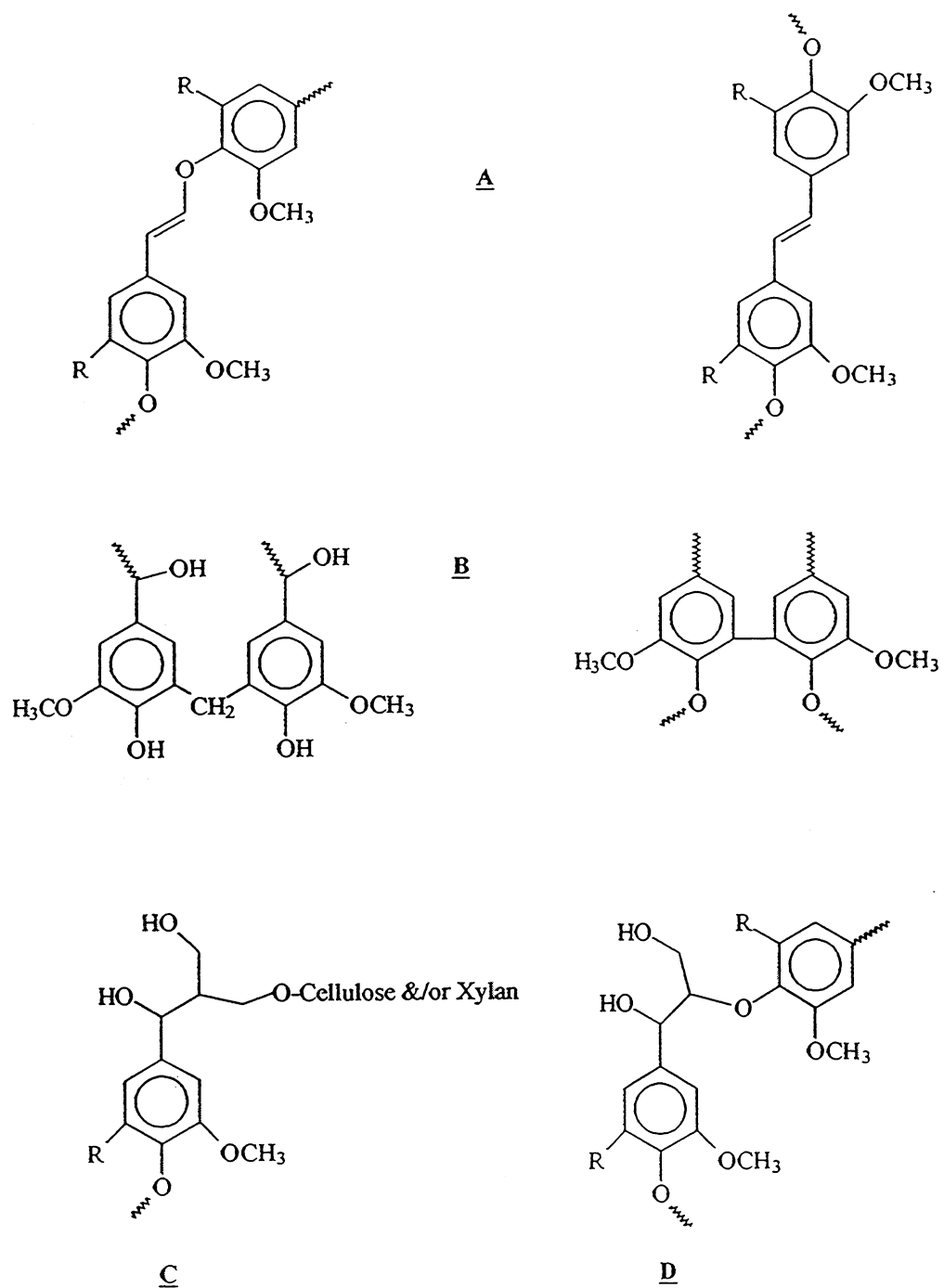
Table 8. Evaluation of Xylanase Pretreatment Procedures for Bleaching Kraft Pulps with 0.5% Charge DMD^a.

<u>Pulp</u>	<u>Degree Delignification (%)</u>	<u>Brightness Gain (%)</u>	<u>Viscosity Loss (%)</u>
<u>Hardwood^b</u>			
W ^c (DMD)E	29	24	22
X ^d (DMD)E	40	31	16
<u>Softwood^e</u>			
W(DMD)E	15	6	14
X(DMD)E	17	6	13

^afreshly prepared 0.1 N DMD/acetone; ^bcommercial northern hardwood, kappa number: 18.0, viscosity: 49.5 Cp; ISO brightness: 34.7; ^cW refers to the control pulp which was washed prior to the DMD stage, this stage which replicates the xylanase treatment (referred to as a X stage) in all parameters, except that the enzyme is not added; ^dthe xylanase stage consisted of treating pulp at 12% consistency, pH 6.0, 50° C with commercial xylanase (ca 85 IU/g of pulp fiber); ^ecommercial northern softwood, kappa number: 27.4, viscosity: 37.0 Cp, ISO brightness: 29.7.

Figure 1.

Chemical Nature of Residual Lignin.



Softwoods: R= H
Hardwoods: R= H, OCH₃

Figure 2.

Overview of DMD Generation and Bleaching Chemistry.

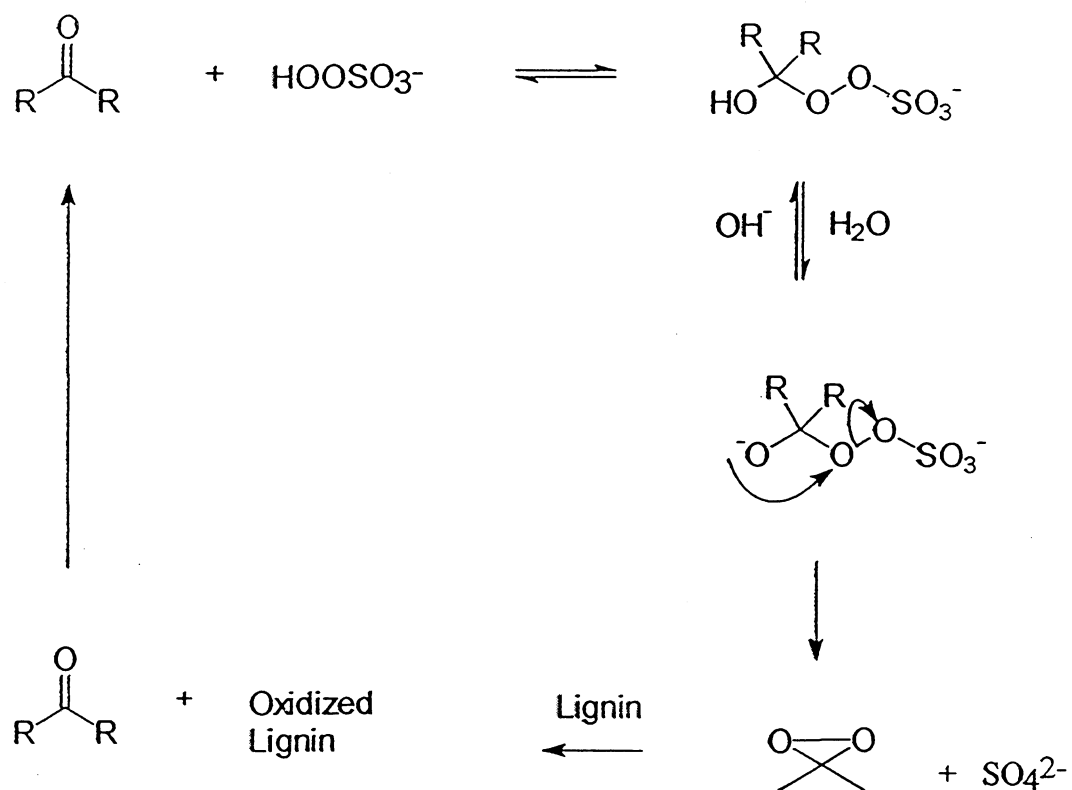
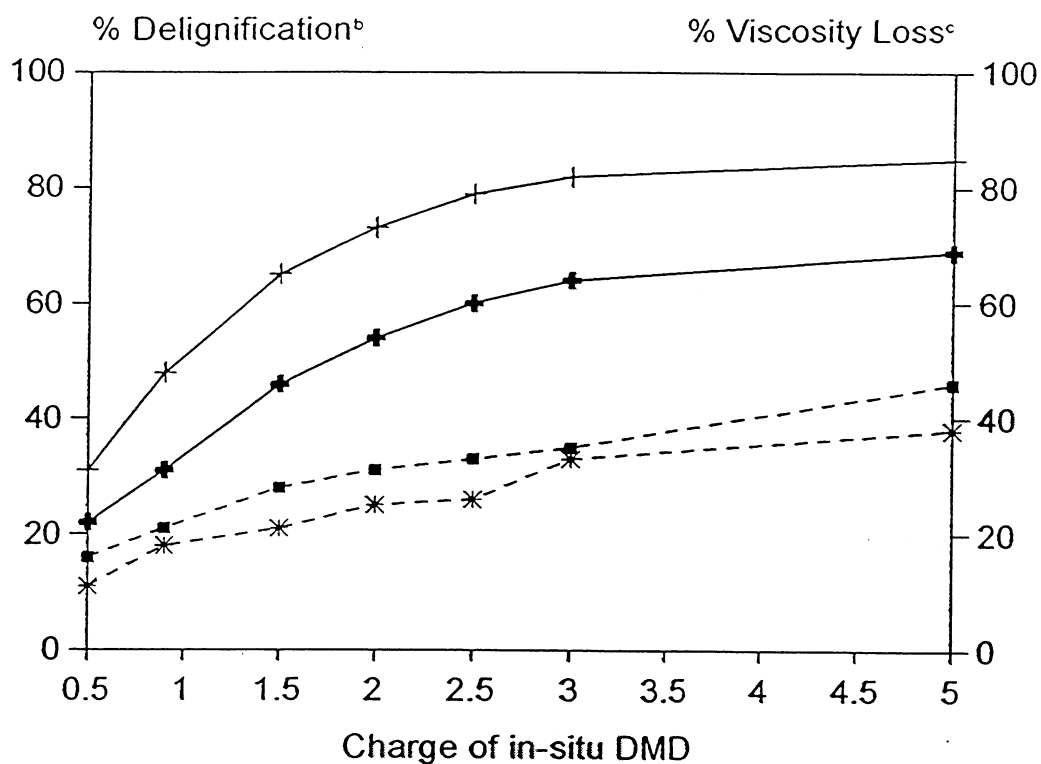


Figure 3.

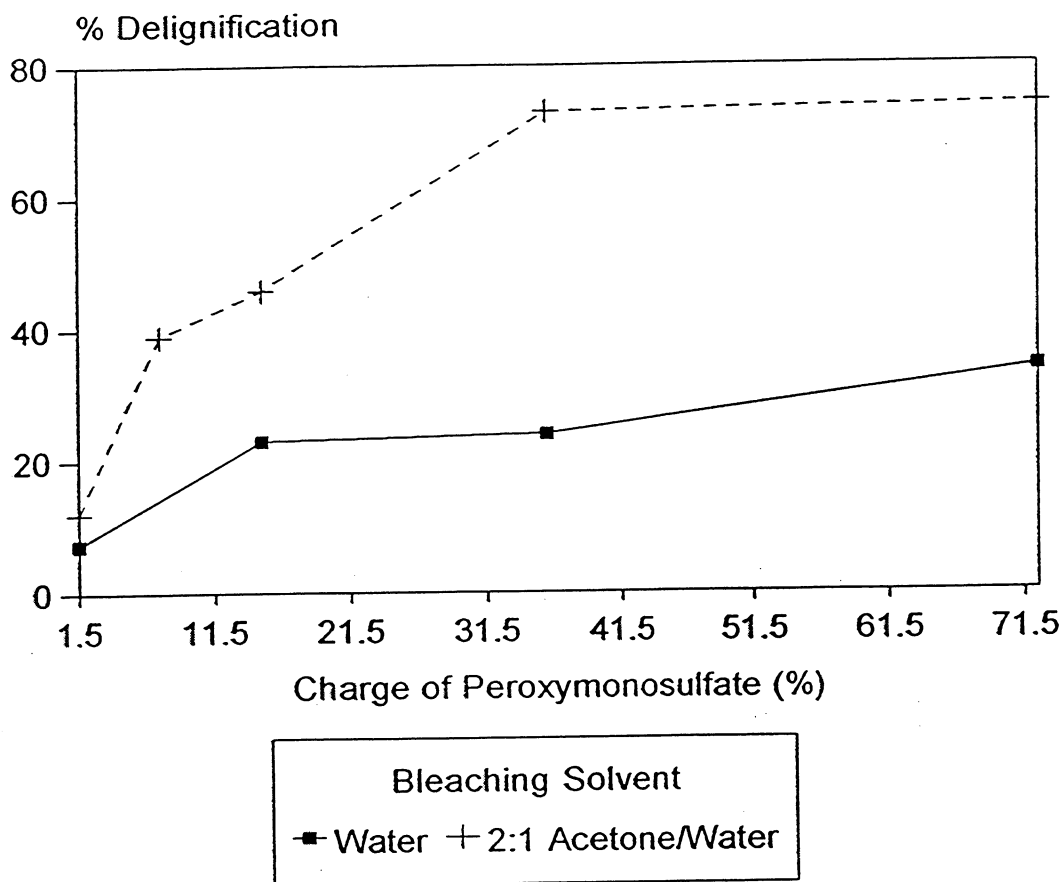
Evaluation of In-Situ DMD Bleaching Efficiency for Western Hemlock Kraft Pulp^a.



+ I (Deg. of Delig.) + IE (Deg. of Delig.) * I (Visc. Loss) ■ IE (Visc. Loss)

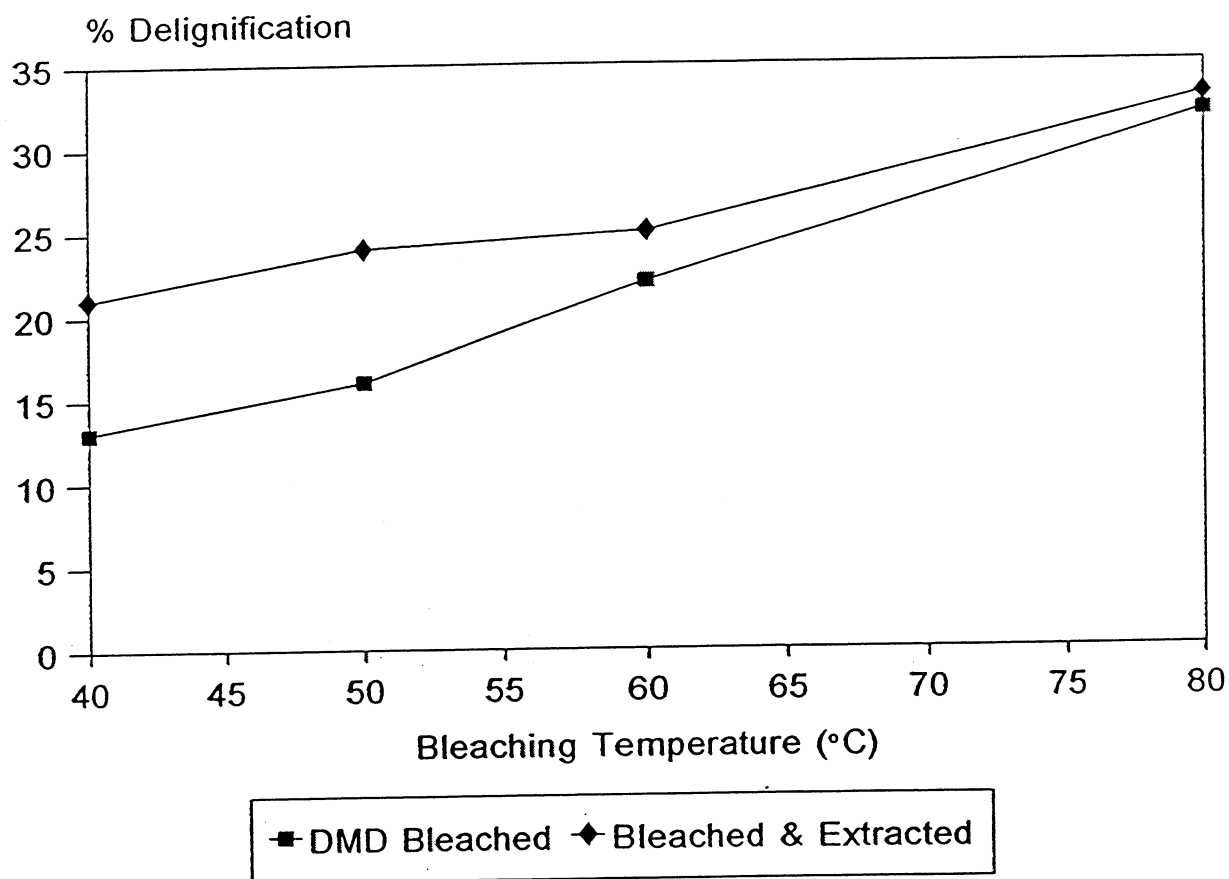
^ainitial kappa: 31.5, viscosity 33.5 mPa.s.; ^b(initial lignin content - final lignin content)/(initial lignin content)%; ^c(initial viscosity - final viscosity)/(initial viscosity) %.

Figure 4. Evaluation of Peroxymonosulfate Bleaching Capabilities Employing Aqueous Acetone and Water Solvent Systems for Softwood Kraft Pulps^a.



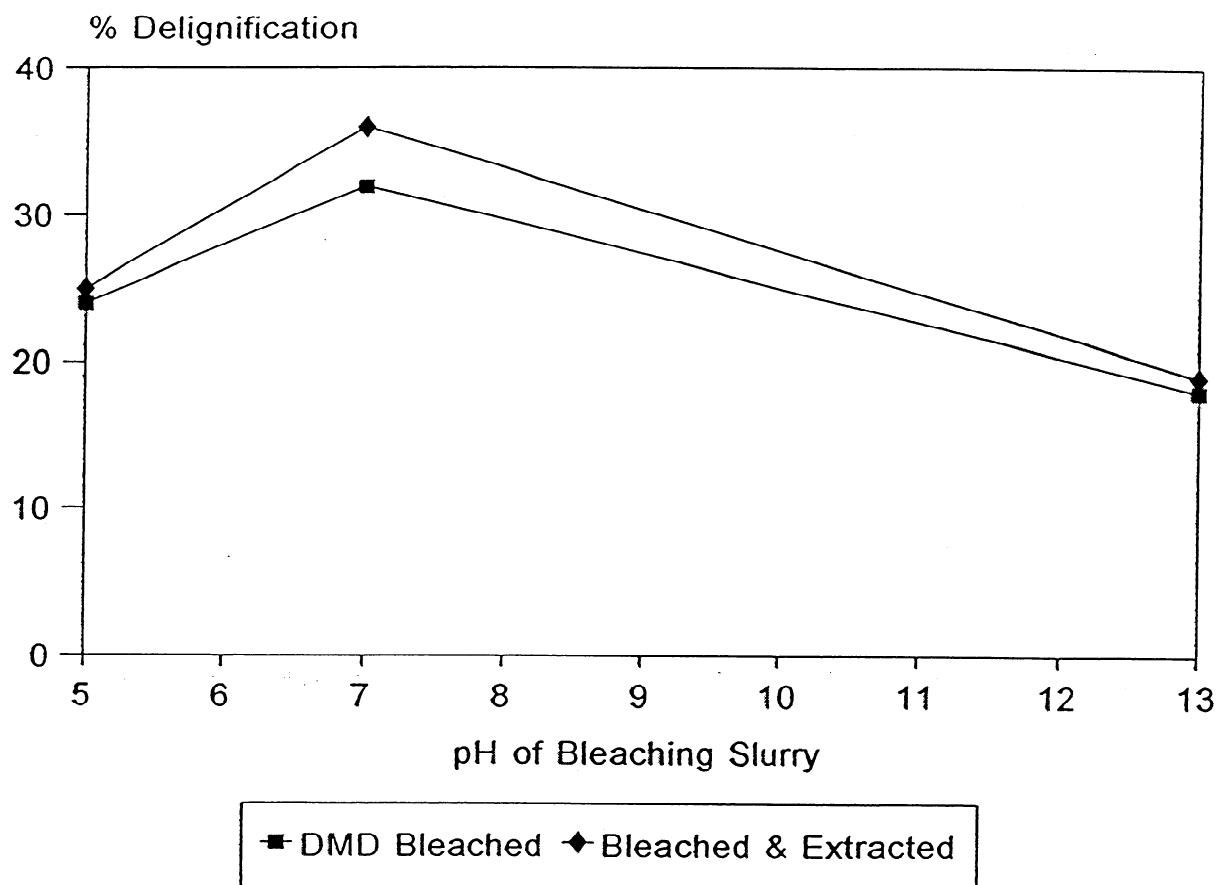
^ainitial kappa: 39.5, viscosity: 38.7 Cp, all bleaching reactions were preformed at RT with stirring.

Figure 5. Effect of Temperature on In-Situ DMD Bleaching^a of Kraft Softwood Pulp.



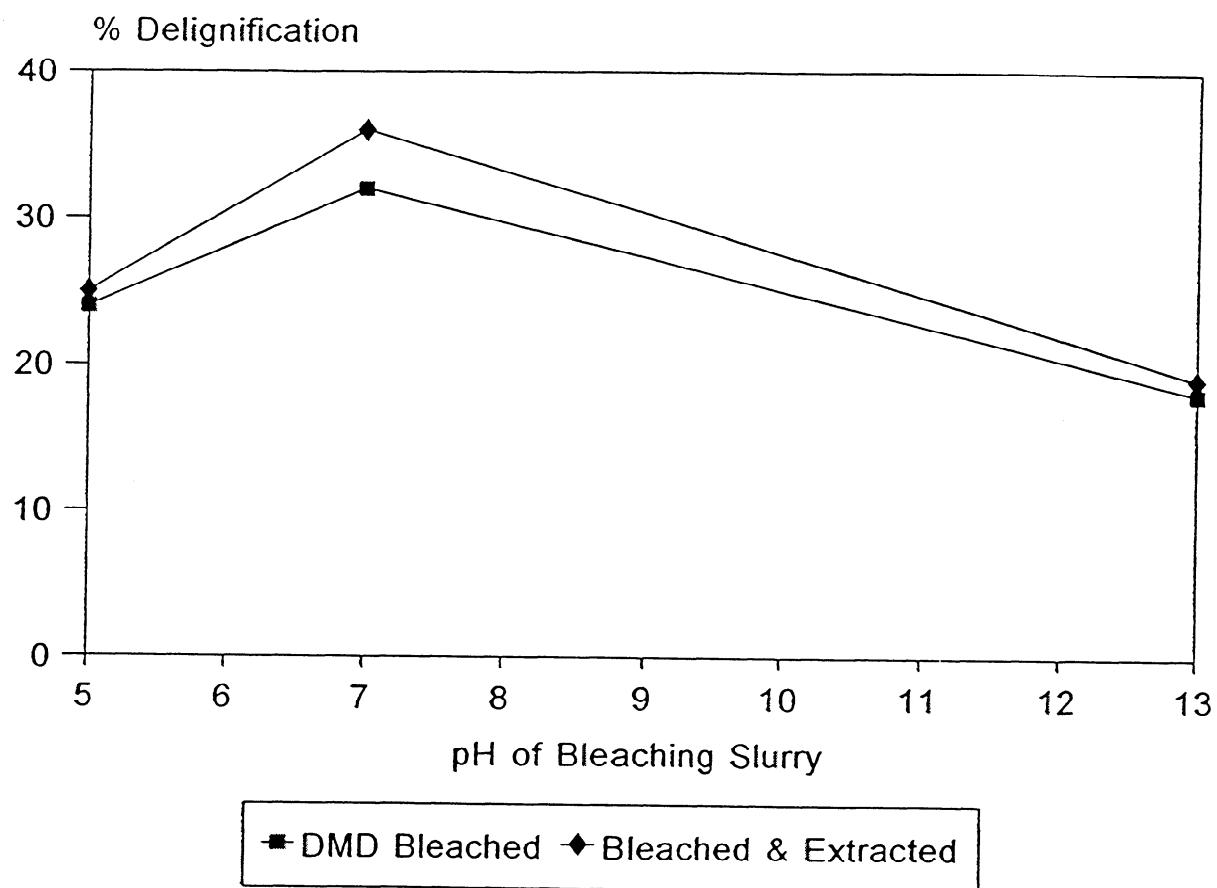
^ainitial kappa: 39.5, viscosity: 38.7 Cp.

Figure 6. Effect of pH on In-Situ DMD Bleaching of Kraft Softwood Pulp^a.



^asee Figure 5 for experimental details.

Figure 6. Effect of pH on in-situ DMD Bleaching of Kraft Softwood Pulp^a



^asee Figure 5 for experimental details

Figure 7.

Typical Brightness Gains For (C/D)ED₁ED₂ Bleaching Sequence

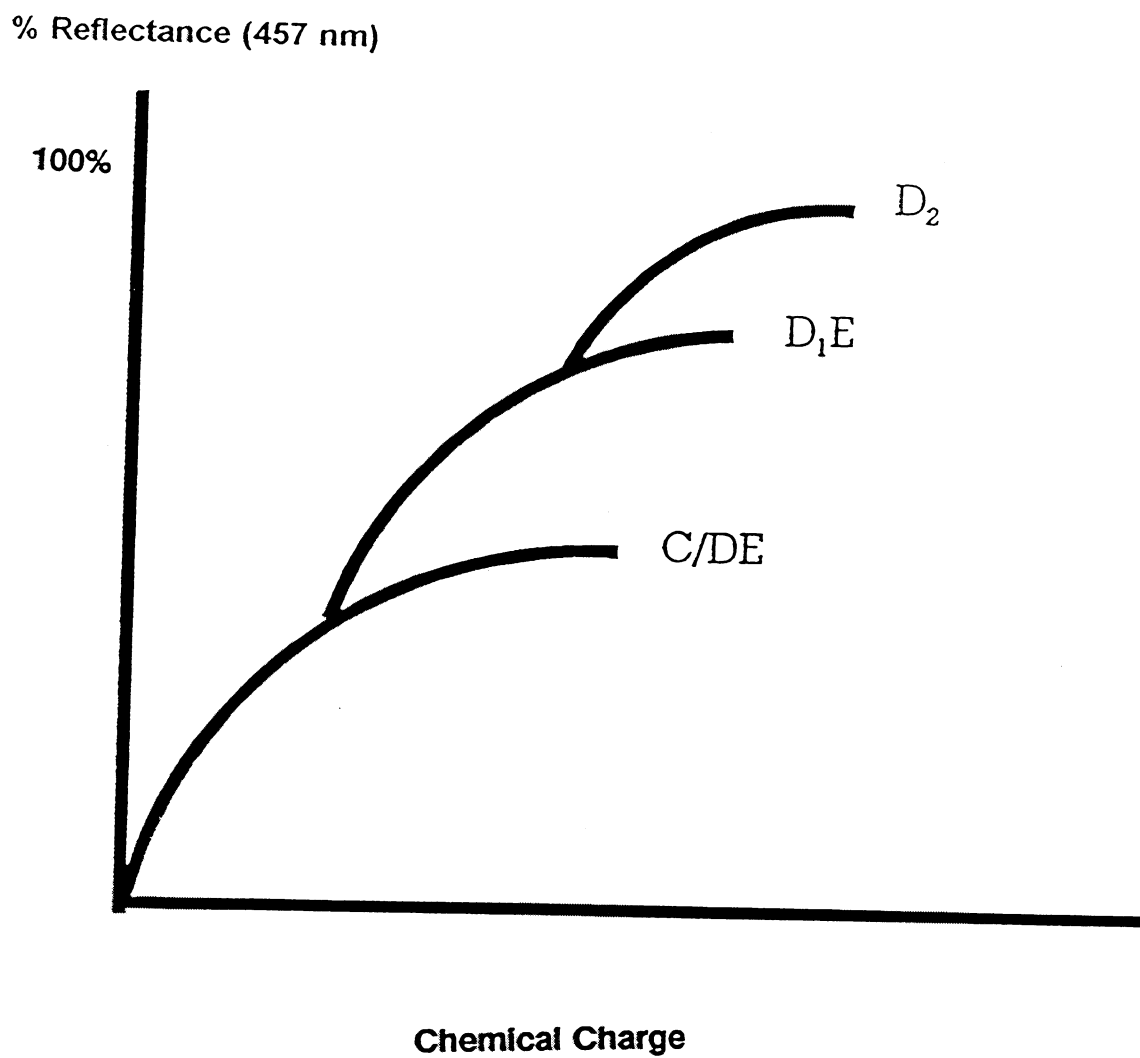
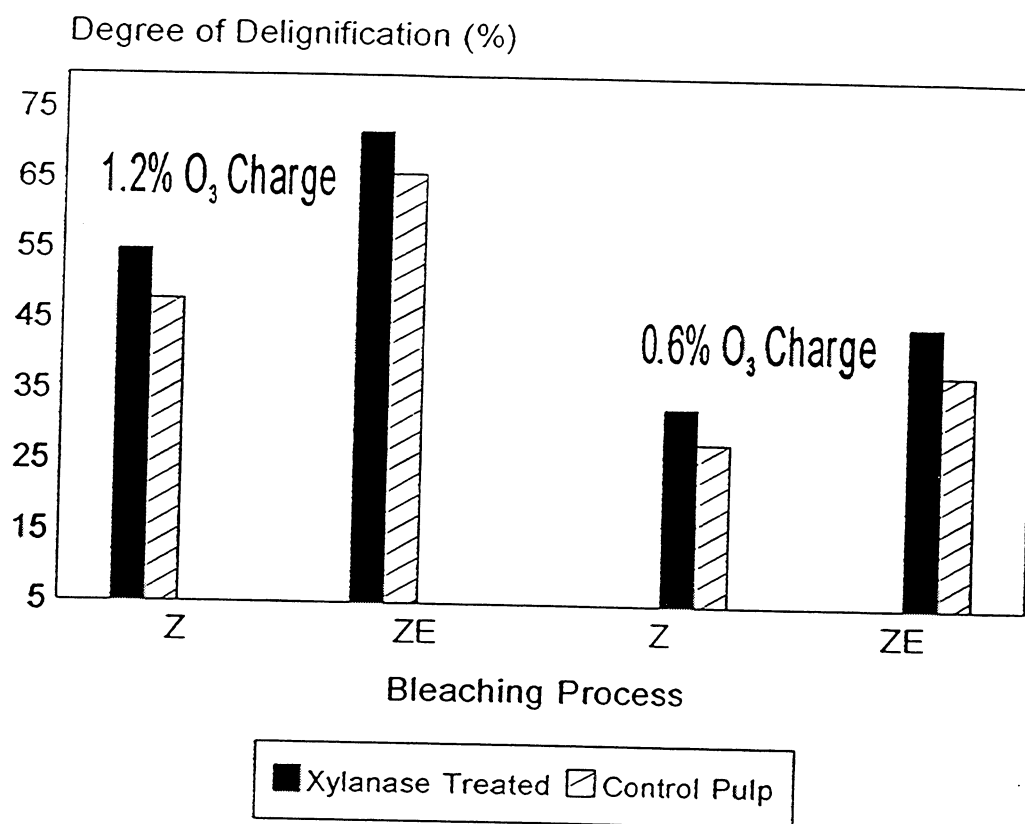


Figure 8. Delignification Benefits of Xylanase-Pretreatment for Bleaching Softwood Kraft Pulp with Xylanase.



REFERENCES

1. Smook, G.A., "Handbook for Pulp and Paper Technologists", TAPPI, Atlanta , GA (1982).
2. "Photochemistry of Lignocellulosic Materials", Heitner, C.; Scaiano, J.C., Ed., ACS Symposium Series 531, ACS (1993).
3. "The Bleaching of Pulp", Singh, R.P., Ed., TAPPI Press, Atlanta, GA (1979).
4. Grier, J., Wood Sci. Technol., 19, 289 (1985).
5. Gellerstedt, G.; Linfors, E.-L., Nordic Pulp Pap. Res. J., 2(2), 71 (1987).
6. Yamasaki, T.; Hosoya, J.S.; Chen, C.-L.; Gratzl, J.S.; Chang, H.M., Proceedings of the 1981 International Symposium on Wood and Pulping Chemistry, Stockholm, 2, 34 (1981).
7. Chiang, V.L.; Funaoka, M., Holzforschung, 42, 385 (1988).
8. Sundquist, J.; Ranua, M.; Hortling, B., Nordic Pulp Paper Res., 33 (1990).
9. Leary, G.J.; Lloyd, J.A.; Morgan, K.R., Holzforschung, 42(3), 199 (1988).
10. Hatch, R.S., "The Bleaching of Pulp", TAPPI Monograph No. 10., First Ed., 78 (1953).
11. Loras, V., In "Pulp and Paper Chemistry and Chemical Technology", 3rd Edition, Casey, J.P., Editor, Wiley-Interscience, NY, 1, 633 (1980).
12. Axegard, P., J. Pulp Paper Science, 12(3), J67 (1986).
13. Weinbauer, J.D.; Thiel, D.A.; Kaczynski, V.W.; Martin, C.S, Proceedings of TAPPI Environmental Conference, 95 (1981).

14. United States Environmental Protection Agency "The National Dioxin Study, Tiers 3,5,6 and 7", EPA 440/4-87-003 Office of Water Regulations and Standards, Washington, D.C., February, 1987.
15. Hise, R.G., Proceedings of 1992 TAPPI Bleach Plant Operations Short Course, 8-1, 201 (1992).
16. Amato, I., Science 261 (5118), 152 (1993).
17. Lierop, B.v.; Liebergott, N.; Faubert, M.G., Proceedings of the 79th CPPA Annual Meeting, Technical Section, B81 (1993).
18. Liebergott, N.; Lierop, B.v.; Skothos, A., Tappi J., February, 117 (1992).
19. McDonough, T.J.; Oxygen delignification. 1989 TAPPI Bleach Plant Operations Seminar Notes. pp 61-69, TAPPI Press Atlanta, 1989.
20. Adam, W.; Curci, R.; Edwards, J.O., Acc. Chem. Res., 22, 205 (1989).
21. Murray, R.W.; Jeyaraman, R.; J. Org. Chem., 50, 2847 (1985).
22. Baumstark, A.L.; Vasquez, P.C., J. Org. Chem., 53, 3437 (1988).
23. Baertschi, S.W.; Raney, K.D.; Stone, M.P.; Harris, T.M., J. Am. Chem. Soc., 110, 7929 (1988).
24. Murray, R.W.; Jeyaraman, R., J. Am. Chem. Soc., 106, 2462 (1984).
25. Adam, W.; Schonberger, A., Tetrahedron Lett., 33(1), 53 (1992).
26. Crandall, J.K.; Zucco, M.; Kirsch, R.S.; Coppert, D.M., Tetrahedron Lett., 32(40), 5441 (1991).
27. "Lignins, Occurrence, Formation, Structure and Reactions", Sarkanen, K.V.; Ludwig, C.H., Ed., John Wiley and Sons, Inc., NY (1971).

28. Murray, R.W.; Jeyaraman, R.; Mohan, L.J., *J. Am. Chem. Soc.*, **108**, 2470 (1986).
29. Marples, B.A.; Muxworthy, J.P.; Baggaley, K.H., *Synlet*, **8**, 646 (1992).
30. Harvey, L.; Ragauskas, A.J., "DMD reactions with lignin-like molecules", manuscript in preparation.
31. Dushin, R.G.; Danishefsky, S.J., *J. Am. Chem. Soc.*, **114**(9), 3471 (1992).
32. Meier, J.; Arnold, G.; Helmling, O., European Patent Application, Application Number: 90115358.5, Date of Filing: 10,08,90.
33. Lee, C.L.; Hunt, K.; Murray, R.W., 1992 TAPPI Pulping Proceedings, 1237 (1992).
34. Ragauskas, A.J., *Tappi J.*, **76**(11), 87 (1993).
35. TAPPI Test Method T-230 om-89, TAPPI Press, Atlanta, GA.
36. TAPPI Test Method T-236 om-85, TAPPI Press, Atlanta, GA.
37. TAPPI Test Method T-452 om-85, TAPPI Press, Atlanta, GA.
38. Lee, C.-L.; PCT, International publication # WO 91/12369, Aug. 22, 1991.
39. a) Lee, C.L.; Hunt, K.; Murray, R.W., *Tappi J.*, **76**(11), 137.
b) Lee, C.L.; Hunt, K.; Murray, R.W., Proceedings from the 7th International Symposium on Wood Pulping and Chemistry, Beijing, China, **1**, 188 (1993).
40. Qui, C.; Senior, D.J.; Rodriguez, A.; Ragauskas, A.J., Proceedings from the 1993 Non-chlorine Bleaching Conference, Hilton Head, SC, 41 (1993).
41. Bryant, P.S.; Robarge, K.; Edwards, L. L., *Tappi J.*, **76**(9), 148 (1993).
42. Lachenal, D.; Bokstrom, M., *J. Pulp Paper Science*, **12**(2), J 50 (1986).
43. Abbot, J., *J. Pulp Paper Science*, **17**(1), J 10 (1991).
44. Springer, E.L.; McSweeney, J.D., *Tappi J.*, **76**(8), 194 (1993).

45. Curci, R.; Edwards, J.O., In "Organic Peroxides", Swern, D., Editor, Wiley-Interscience 1, Chap. 4, 199 (1970).
46. Santiago, D.; Rodriguez, A.; Ragauskas, A.J., "Examination of Trace Metals on DMD Bleaching Properties", manuscript in preparation.
47. Basta, J.; Holtinger, L.; Hook, J., Proceedings from the 6th International Symposium on Wood and Pulp Chemistry, Melbourne, 237 (1991).
48. Earl, P.F.; Nguyen, X.T., Proceedings from the 1993 Non-Chlorine Bleaching Conference, Hilton Head, SC, 32 (1993).
49. Montgomery, R.E., J. Am. Chem. Soc., 96, 7820 (1974).
50. Ragauskas, A.J.; Szwec, J., " Bleaching Kraft Pulps with Dimethyldioxirane and Other Substituted Dioxiranes", manuscript submitted for publication.
51. Curci, R.; Fiorentino, M.; Troisi, L., J. Org. Chem., 45, 4758 (1980).
52. Reeve, D.W., 1989 Bleach Plant Operations, TAPPI Seminar Notes, 1, (1989).
53. Ljunggren, S.; Johansson, E., Holzforschung, 44, 291 (1990).
54. McDonough, T.J.; Marquis, A.; Ragauskas, A.J., "Totally Chlorine Free Bleaching with Dimethyldioxirane", paper accepted for 1994 International Pulp Bleaching Conference, Vancouver Canada.
55. Paice, M.G.; Gurnagul, N.; Page, D.H.; Jurasek, L., Enzyme Microb. Technol., 14, 272 (1992)
56. Senior, D.J.; Hamilton, J., J. Pulp and Paper Science, 18(5), J165 (1992).
57. Ragauskas, A.J.; Poll, K.; Cesterinno, A.J., Enzyme Microb. Technol., 16, 1 (1994).

58. Kantelinen, A.; Hortling, B.; Sundquist, J.; Linko, M.; Viikari, L., *Holzforschung*, 47, 318 (1993).

